On the Absence of a Diffuse Double Layer at Electronically Conductive Polymer Film Electrodes. Direct Evidence by Atomic Force Microscopy of Complete Charge Compensation

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Although electrodes of electronically conductive polymers, like polythiophenes or polypyrroles,[1−5] are often described as showing metallic behavior, in fact there have been few studies that address the question of electrode surface charge as a function of potential.[6−10] While the conductivity of the polymer films is clearly electronic over a given potential range, one can also consider how the charge is distributed in the film and at the film/solution interface. We show here that there are significant differences between conductive polymer and metal electrodes. During electrochemical oxidation and reduction of the polymer film, there is a flux of ions in to and out of the film to compensate for the charge in the film.[10−13] In this communication we provide direct evidence by atomic force microscopy (AFM) measurements of complete charge compensation in poly(3-methylthiophene) and polypyrrole films. This total compensation suggests that there is no diffuse double layer at the conductive polymer/solution interface, a situation distinctly different than that at metal or semiconductor electrodes.

We have employed the in situ AFM/electrochemical technique to study the electronically conductive polymer film/aqueous solution interface. This method has been well documented.[14−16] Briefly, a standard AFM cantilever with a silicon nitride tip was modified by the attachment of a silica sphere with a diameter of 10 to 20 μm. At pH values above 3 the silica surface is negatively charged by deprotonation of surface OH groups and OH^- adsorption. The charge on the silica surface can be determined by measuring the force curve between the AFM cantilever and a silica substrate.[14] When the negatively charged tip approaches a sample surface that is also negatively charged, a repulsive force curve is obtained. When the sample surface is positive, an attractive force curve is observed. Thus one can distinguish the nature of the surface charge by noting the AFM force curve in solution and find the magnitude of the surface charge by comparing the measured curve to a theoretical one based on diffuse double-layer theory.[14−16]

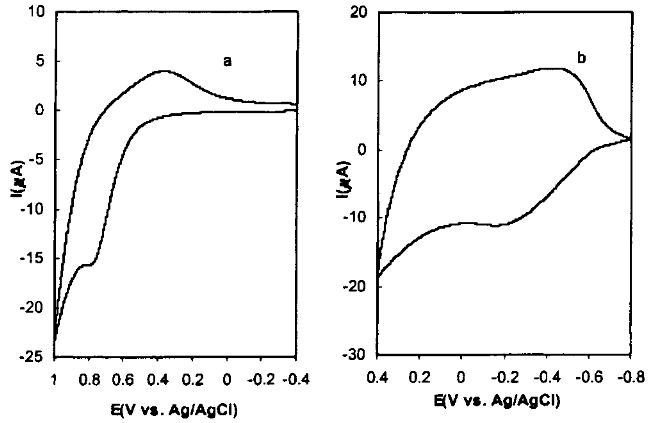

Figure 1. Cyclic voltammograms of (a) poly(3-methylthiophene) and (b) polypyrrole on a Pt substrate in 0.01 M $KClO_4$; scan rate, 0.1 V/s. Polymer films had an area of 0.031 cm^2 and were about 100 nm thick.

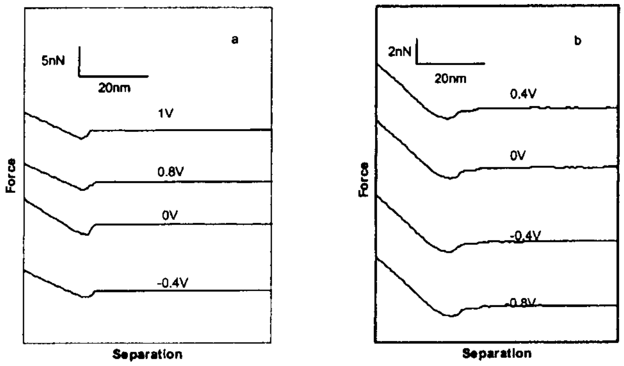

Figure 2. Forces between the silica sphere and the conductive polymer film in 0.001 M $KClO_4$ as a function of electrode potential: (a) poly(3-methylthiophene) and (b) polypyrrole.

In this study, the potential of the electrode in an AFM liquid cell with reference (Ag/AgCl) and counter (Pt) electrodes was controlled by a potentiostat. The conductive polymer films were prepared by anodic sweeps of the Au substrate in solutions of the monomer in MeCN, maintained in the reduced state, and then transferred to the AFM liquid cell for in situ measurements with an aqueous electrolyte. The surface roughness of the films, as determined by AFM, was about 3 nm (RMS) over an area of 1 μm^2. The potential of the electrode was controlled at different potentials encompassing the region where the film was in the reduced and oxidized forms and the AFM force curve was obtained with the electrode under potential control.

The cyclic voltammograms of poly(3-methylthiophene) and polypyrrole in 0.01 M $KClO_4$ are shown in Figure 1. The behavior is typical of oxidation to the conductive form (peaks at about 0.75 V and −0.25 V, respectively) and reduction to the nonconductive form. Figure 2a shows the force curves for the poly(3-methylthiophene) film in 0.001 M $KClO_4$ at different potentials. This behavior can be contrasted with that for a gold electrode of about the same roughness (Figure 3). The force curves are somewhat noisier, but of the same general shape as that of a smooth gold electrode (shown in the Supporting Information along with AFM images of the gold and polymer surfaces, Figures S3−S5). At a potential of −0.4 V, the film is in the reduced (uncharged) state, so that no diffuse double layer exists at the film/solution interface, and there is no electrostatic force between the tip and the polymer film. The force curve is flat until the tip

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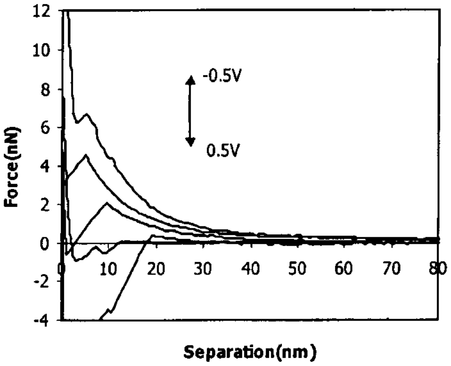

Figure 3. Forces between the silica probe and an electrochemically roughened Au electrode in 0.001 M $KClO_4$ as a function of electrode potential. The force curves correspond to controlled potentials of, from top to bottom, −0.5, −0.3, 0, 0.2, and 0.5 V vs Ag/AgCl. The electrochemical roughening of the electrode consisted of successive anodic−cathodic potential scans in 0.1 M KCl from −0.3 to 1.2 V for 25 cycles at 500 mV/s, holding the potential for about 2 s at the positive limit during each cycle.

reaches distances where van der Waals forces cause a jump to contact, and further approach of the sample just moves the cantilever in a linear way. When the potential is made more positive, so that the film is oxidized, the observed behavior is the same. In this case the positive charge in the film is compensated completely by solution anions (ClO_4^-). If only partial compensation of the positive film charge had occurred, there would be residual charge that would have resulted in an attractive force curve. Indeed this uncharged behavior is observed independent of the electrode potential up to +1 V vs Ag/AgCl.

The same behavior is found with a polypyrrole film (Figure 2b). There is no indication of electrostatic attraction or repulsion over the film potential region of +0.4 to −0.8 V vs Ag/AgCl. Again the charge in the film during polypyrrole oxidation is completely compensated by anions. In the 0.001 M $KClO_4$ solution, the Debye length is about 9.6 nm. Since the surface roughness of the film is about 3 nm (RMS) over an area of 1 μm^2, it is possible that the roughness of the film affected the measurements. However, the approach curves were the same at different locations on the surface (AFM scans and surface section analysis are given in Figures S1 and S2). The same results were obtained in a 0.01 M $KClO_4$ solution (where the Debye length is about 3 nm) for both polymers (Figure S6).

Thus the results of this study clearly indicate that the behavior of conductive polymer electrodes is qualitatively different from that of metal electrodes (Figure 4). With metals, excess charge builds up on the metal surface when the potential is moved from the point of zero charge and this surface charge is largely compensated by the diffuse double layer at the interface. When the electrode is charged negative, the AFM cantilever with the negative silica sphere is repelled during a force curve. When the electrode is positive, the cantilever is attracted. A detailed discussion of such curves at a gold electrode will be presented elsewhere.[16] With the polymer electrodes, all of the charge is compensated by solution ions that can penetrate the polymer matrix either within the polymer strands or in pores in the polymer. When a neutral polymer is made positive, anions compensate the charge, at least over a large range of potential. When the oxidized polymer is made more negative, anions are released and cations move into the lattice, again totally compensating the charge. Ions may also form a compact layer at the solution interface. However, in aqueous solutions over the range of potentials usually of interest with polymer electrodes, no diffuse double layer exists at the interface.

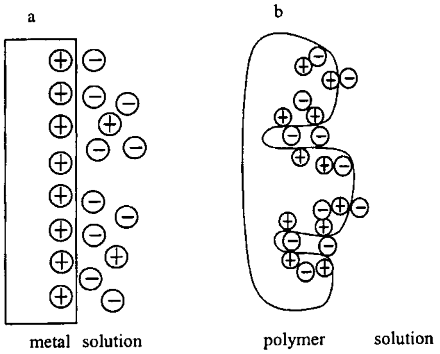

Figure 4. Illustration of the electrode/solution interface structure for (a) metal and (b) conductive polymer film electrodes.

In interpretation of the capacitance of conductive polymer films, one cannot separate the faradaic and capacitive current components.[17] Thus, a description of the details of where the counterions reside during charging cannot be obtained from capacitance measurements. The implications of the results here is that they mainly reside within the polymer film and that any electrode capacitance that could be ascribed to the film would be an inner or compact layer capacitance. An alternative view, suggested by a reviewer, is that the ionic concentration is so high within the polymer pores that all of the compensation occurs in a compact and extremely thin (a few angstroms) diffuse layer. Note that the behavior of these electronically conductive films is also different from that of films of polyelectrolytes, which will be described elsewhere.

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Supporting Information Available: Cyclic voltammograms, force curves, and AFM images of the polymer and gold films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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